Supporting Information

Palladium-catalysed coupling of α-halo vinylphosphonate and α-phosphonovinyl sulfonate with alkylzincs: straightforward and versatile synthesis of α-alkyl vinylphosphonates

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General information

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. DMA and toluene were distilled over CaH$_2$ prior to use. Zinc power was activated by washing with a dilute HCl solution.$^{[1]}$ Alkyl bromide, benzyl chloride, and dimethylzinc were obtained from commercial sources and used without further purification unless otherwise noted. Organozinc reagents,$^{[2]}$ $\alpha$-halo vinylphosphonates,$^{[3]}$ and $\alpha$-phosphonovinyl sulfonates$^{[4]}$ were synthesized according to the published procedures. The concentration of the resulting organozinc reagents were determined by iodiometric titration.$^{[5]}$

NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz). Chemical shifts were reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (CDCl$_3$, $\delta_H = 7.26$, $\delta_C = 77.0$). Spectra were reported as follow: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on ESI-Q-TOF spectrometer (Bruker microTOF-Q II).

Procedure for the preparation of alkylzinc bromide (2a-m, 5)

A dry 25 mL Schlenk-flask was heated with a heat gun (350 °C) for 10 min under high vacuum. After cooling to room temperature, the flask was flushed with nitrogen (repeated 3 times). Then, Zinc power (975 mg, 15 mmol), I$_2$ (127 mg, 0.5 mmol) and dry DMA (10 mL) was added. Stirring the mixture until the red color of I$_2$ disappeared, alkylic bromide (10 mmol) was added and stirred at 80 °C for 3-4 h.

Procedure for the preparation of benzylic zinc chloride (4a-l)

A dry 25 mL Schlenk-flask was heated with a heat gun (350 °C) for 10 min under high vacuum. After cooling to room temperature, the flask was flushed with nitrogen (repeated 3 times). Then, Zinc power (1.5-2.0 equiv), I$_2$ (127 mg, 0.5 mmol) and dry DMA (10 mL) was added. Stirring the mixture until the red color of I$_2$ disappeared, benzylic chloride (10 mmol) was added and stirred at the required temperature (40-80 °C) for 4 h.

General procedure for the synthesis of 3a-l, 3n, 6a-m, 7, 9, 11, 13, 15, 17 via Pd-catalysed Negishi cross-coupling

A Schlenk-flask was loaded with $\alpha$-(pseudo)halo vinylphosphonate (0.4 mmol), Pd(OAc)$_2$ (4.5 mg, 0.02 mmol), SPhos (16.4 mg, 0.04 mol). The flask was held under vacuum for 10 min and filled with nitrogen (repeated 3 times). DMA (1 mL) was introduced and the mixture was stirred. Alkylzinc bromide (1.2-1.4 equiv) or benzylic zinc chloride (1.1-1.2 equiv) was added dropwise at room temperature and stirred at 40 °C for 1-3 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and quenched with saturated NH$_4$Cl (1 mL) and 1 N HCl (2 mL), and the mixture was extracted with EtOAc (4 × 4 mL). The combined organic phase was washed with brine, dried over anhydrous Na$_2$SO$_4$ overnight, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (1/1, v/v) as the eluent to gave the cross-coupling product $\alpha$-substituted vinylphosphonate as a pale yellow oil.

The synthesis of 3m via Ni-catalysed Negishi cross-coupling of $\alpha$-bromovinylphosphonate (1a)
with pent-4-en-1-ylzinc bromide (2m)

A Schlenk-flask was loaded with diethyl α-bromo vinylphosphonate (97.2 mg, 0.4 mmol), NiCl₂(dppp) (21.6 mg, 0.04 mol). The flask was held under vacuum for 10 min and filled with nitrogen (repeated 3 times). Then DMA (1 mL) was introduced and the mixture was stirred. The pent-4-en-1-ylzinc bromide (1.2 equiv) was added dropwise at room temperature and stirred at 40 °C for 3 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and quenched with saturated NH₄Cl (1 mL) and 1 N HCl (2 mL), and the mixture was extracted with EtOAc (4 × 4 mL). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄ overnight, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (1/1, v/v) as the eluent to gave diethyl hepta-1,6-dien-2-ylphosphonate 3m (68.7 mg, 74%) as a colorless oil.

The synthesis of 19 via Pd-catalysed Negishi cross-coupling of diethyl α-bromo vinylphosphonate (1a) with dimethylzinc reagent

A Schlenk-flask was loaded with diethyl α-bromo vinylphosphonate (4.86 g, 20 mmol), Pd(OAc)₂ (224.5 mg, 1.0 mmol), SPhos (820 mg, 2.0 mmol). The flask was held under vacuum for 10 min and then filled with nitrogen (repeated 3 times). Then toluene (88 mL) was introduced and the mixture was stirred. The dimethylzinc (1 M in toluene, 12 mL, 1.2 equiv) was added dropwise at 0 °C and then stirred at 40 °C for 6 h. Upon completion of the reaction, the resulting mixture was cooled down to room temperature and quenched with saturated NH₄Cl (30 mL), and the mixture was extracted with EtOAc (4 × 30 mL). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄ overnight, filtered, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum ether/EtOAc (1/1, v/v) as the eluent to gave the cross-coupling product α-methyl vinylphosphonate 19 (1.61g, 45%) as a pale yellow oil.

General procedure for the diimide reduction of alkenylphosphonates to access 1-alkylethylphosphonates (20a-f)

A Schlenk flask was loaded with diethyl α-substituted vinylphosphonate (82.2 mg, 0.3 mmol), NBSH (130.0 mg, 0.6 mmol), K₃PO₄ (63.6 mg, 0.3 mmol) and held under vacuum for 10 min and then filled with nitrogen. Then CH₂CN (2.0 mL) was introduced and the mixture was stirred at rt for 5-6 h. After completion of the reaction, the mixture was added water (3 mL), and extracted with EtOAc (4 × 3 m L). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄ overnight, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel column using petroleum ether/EtOAc (1/1, v/v) as eluent to give 1-alkylethylphosphonates (20a-f) as an oil.

Characterizations of new compounds

Diisopropyl (1-chlorovinyl)phosphonate (1f). Pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 1.35 (d, J = 6.2 Hz, 6H), 1.38 (d, J = 6.2 Hz, 6H), 4.67-4.76 (m, 2H), 6.12 (dd, J = 35.7 Hz, 1.3 Hz, 1H), 6.43 (dd, J = 13.3 Hz, 1.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 23.6 (d, J = 5.1 Hz), 24.0
(d, J = 3.8 Hz), 72.3 (d, J = 5.7 Hz), 130.2 (d, J = 16.7 Hz), 131.8 (d, J = 206.3 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): δ 5.7; IR (neat): ν (cm$^{-1}$) 3756, 3343, 2936, 2899, 2856, 1464, 1261, 991; GC-MS: m/z (rel intensity) 227 (M+H$^+$, 4), 185 (18), 169 (76), 144 (100), 124 (22), 107 (21), 98 (12), 81 (12); HRMS (ESI) C$_8$H$_{17}$ClO$_3$P [M+H$^+$] 227.0598, found 227.0611.

Ethyl 5-(diethoxyphosphoryl)hex-5-enoate (3a). Pale yellow oil (93.4 mg, 84% yield); $^1$H NMR (500 MHz, CDCl$_3$): δ 1.24-1.27 (m, 3H), 1.32 (t, J = 7.1 Hz, 6H), 1.84-1.90 (m, 2H), 2.26-2.34 (m, 4H), 4.05-4.15 (m, 6H), 5.78 (d, J = 48.6 Hz, 1H), 6.06 (d, J = 22.9 Hz 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 14.2, 16.3 (d, J = 6.3 Hz), 23.2 (d, J = 5.4 Hz), 31.5 (d, J = 11.1 Hz), 33.5, 60.3, 61.8 (d, J = 5.7 Hz), 129.6 (d, J = 9.5 Hz), 138.5 (d, J = 171.1 Hz), 173.2; $^{31}$P NMR (202.5 MHz, CDCl$_3$): δ 19.3; IR (neat): ν (cm$^{-1}$) 3482, 2938, 2897, 2843, 1732, 1464, 1253, 1053, 1024, 966; LC-MS (ESI) [M+H$^+$]: 279.29; HRMS (ESI) calcd for C$_{12}$H$_{23}$NaO$_3$P [M+Na$^+$] 299.1747, found 299.1750.

Diethyl dec-1-en-2-ylphosphonate (3c). Pale yellow oil (83.9 mg, 76% yield); $^1$H NMR (500 MHz, CDCl$_3$): δ 0.88 (t, J = 7.1 Hz, 6.8 Hz, 3H), 1.25-1.34 (m, 16H), 1.48-1.54 (m, 2H), 2.20-2.26 (m, 2H), 4.02-4.13 (m, 4H), 5.75 (dd, J = 49.1 Hz, 1.6 Hz, 1H), 6.02 (d, J = 23.1 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 14.1, 16.3 (d, J = 6.3 Hz), 22.6, 27.9 (d, J = 5.7 Hz), 29.1, 29.2, 29.3, 31.8, 32.1 (d, J = 10.8 Hz), 61.7 (d, J = 5.8 Hz), 128.8 (d, J = 9.6 Hz), 139.4 (d, J = 169.6 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): δ 20.0; IR (neat): ν (cm$^{-1}$) 3480, 2938, 2897, 2843, 1732, 1464, 1258, 1055, 1028, 962; LC-MS (ESI) [M+H$^+$]: 277.34; HRMS (ESI) calcd for C$_{14}$H$_{29}$NaO$_3$P [M+Na$^+$] 299.1747, found 299.1750.

Diethyl hept-1-en-2-ylphosphonate (3d). Pale yellow oil (82.4 mg, 88% yield); $^1$H NMR (500 MHz, CDCl$_3$): δ 0.89 (t, J = 6.8 Hz, 3H), 1.29-1.35 (m, 10H), 1.49-1.55 (m, 2H), 2.20-2.26 (m, 2H), 4.02-4.13 (m, 4H), 5.75 (dd, J = 49.1 Hz, 1.0 Hz, 1H), 6.02 (d, J = 23.1 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 13.9, 16.3 (d, J = 6.3 Hz), 22.4, 27.5 (d, J = 5.4 Hz), 31.3, 32.0 (d, J = 10.7 Hz), 61.6 (d, J = 5.6 Hz), 128.8 (d, J = 9.3 Hz), 139.4 (d, J = 169.6 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): δ 19.9; IR (neat): ν (cm$^{-1}$) 3476, 2936, 2901, 2857, 1464, 1257, 1026, 960, 792; GC-MS: m/z (rel intensity) 235 (M+H$^+$, 10), 205 (44), 191 (29), 177 (74), 149 (100), 135 (53), 95 (44), 81 (44), 98 (12), 81 (12); HRMS (ESI) C$_{11}$H$_{23}$NaO$_3$P [M+Na$^+$] 257.1277, found 257.1288.
Diethyl (3-cyclohexylprop-1-en-2-yl)phosphonate (3f). Pale yellow oil (92.6 mg, 89% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.80-0.89 (m, 2H), 1.09-1.27 (m, 3H), 1.32 (t, $J = 7.1$ Hz, 6H), 1.56-1.74 (m, 6H), 2.12 (dd, $J = 15.9$ Hz, 7.1 Hz, 2H), 4.01-4.12 (m, 4H), 5.70 (dd, $J = 48.9$ Hz, 1.4 Hz, 1H), 6.05 (dd, $J = 22.8$ Hz, 1.3 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J = 6.4$ Hz), 26.2, 26.5, 33.0, 35.7 (d, $J = 3.5$ Hz), 40.6 (d, $J = 10.8$ Hz), 61.6 (d, $J = 5.9$ Hz), 130.3 (d, $J = 9.7$ Hz), 137.6 (d, $J = 169.2$ Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.9; IR (neat): $\nu$ (cm$^{-1}$) 3483, 2938, 2897, 2843, 1464, 1226, 1026, 961; GC-MS: m/z (rel intensity) 260 (M$^+$, 12), 178 (84), 150 (100), 122 (89), 96 (46), 82 (29); HRMS (ESI) calcd for C$_{13}$H$_{26}$O$_3$P [M+H]$^+$ 261.1541, found 261.1545.

Diethyl (5-phenylpent-1-en-2-yl)phosphonate (3h). Pale yellow oil (86.9 mg, 77% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.31 (t, $J = 7.1$ Hz, 6H), 1.83-1.89 (m, 2H), 2.26-2.32 (m, 2H), 2.64 (t, $J = 7.7$ Hz, 2H), 4.01-4.13 (m, 4H), 5.77 (d, $J = 48.9$ Hz, 1.5 Hz, 1H), 6.05 (d, $J = 23.0$ Hz, 1H), 7.17-7.20 (m, 3H), 7.27-7.30 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.2 (d, $J = 6.3$ Hz), 29.6 (d, $J = 5.4$ Hz), 31.7 (d, $J = 10.8$ Hz), 35.2, 61.7 (d, $J = 5.7$ Hz), 125.8, 128.26, 128.32, 129.2 (d, $J = 9.4$ Hz), 138.9 (d, $J = 170.3$ Hz), 141.8; $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.7; IR (neat): $\nu$ (cm$^{-1}$) 3502, 2938, 2895, 2843, 1712, 1463, 1254, 1053, 1026, 964; LC-MS (ESI) [M+H]$^+$: 283.19; HRMS (ESI) calcd for C$_{15}$H$_{24}$O$_3$P [M+H]$^+$ 283.1458, found 283.1468.

Diethyl (5-(1,3-dioxoisoindolin-2-yl)pent-1-en-2-yl)phosphonate (3i). Pale yellow oil (56.2 mg, 56% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.31 (t, $J = 7.1$ Hz, 6H), 1.90-1.96 (m, 2H), 2.29-2.34 (m, 2H), 3.70-3.73 (m, 2H), 4.02-4.13 (m, 4H), 5.83 (dd, $J = 48.6$ Hz, 1.4 Hz, 1H), 6.07(dd, $J = 23.0$ Hz, 0.9 Hz, 1H), 7.71-7.73 (m, 2H), 7.84-7.85 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J = 6.2$ Hz), 16.9, 24.7, 26.9 (d, $J = 5.2$ Hz), 123.2, 129.7 (d, $J = 9.3$ Hz), 132.0, 134.0, 138.0 (d, $J = 171.8$ Hz), 168.3; $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.2; IR (neat): $\nu$ (cm$^{-1}$) 3464, 2937, 2897, 2843, 1712, 1464, 917; LC-MS (ESI) [M+H]$^+$: 252.37; HRMS (ESI) calcd for C$_{17}$H$_{22}$NNaO$_5$P [M+Na]$^+$ 374.1128, found 374.1152.

Diethyl (6-cyanohex-1-en-2-yl)phosphonate (3j). Pale yellow oil (86.2 mg, 88% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.32 (t, $J = 7.1$ Hz, 6H), 1.70 (br, 4H), 2.28-2.31 (m, 2H), 2.37-2.38 (m, 2H), 4.05-4.12 (m, 4H), 5.76 (dd, $J = 48.4$ Hz, 1.2 Hz, 1H), 6.04 (d, $J = 22.8$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J = 6.2$ Hz), 16.9, 24.7, 26.9 (d, $J = 5.2$ Hz), 31.4 (d, $J = 11.0$ Hz), 61.8 (d, $J = 5.8$ Hz), 119.4, 129.4 (d, $J = 9.2$ Hz), 138.3 (d, $J = 171.8$ Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.1; IR (neat): $\nu$ (cm$^{-1}$) 3447, 2936, 2899, 2843, 1464, 1223, 1051, 1024, 966;
5-(Diethoxyphosphoryl)hex-5-en-1-yl acetate (3k). Pale yellow oil (93.4 mg, 80% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.32 (t, $J$ = 7.1 Hz, 6H), 1.37-1.43 (m, 2H), 1.53-1.59 (m, 2H), 1.62-1.68 (m, 2H), 2.04 (s, 3H), 2.22-2.28 (m, 2H), 4.01-4.13 (m, 6H), 5.75 (dd, $J$ = 48.9 Hz, 1.4 Hz, 1H), 6.03 (d, $J$ = 22.9 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J$ = 6.1 Hz), 20.9, 25.4, 27.5 (d, $J$ = 5.2 Hz), 28.3, 31.9 (d, $J$ = 10.8 Hz), 61.7 (d, $J$ = 5.5 Hz), 64.3, 129.0 (d, $J$ = 9.4 Hz), 139.0 (d, $J$ = 170.5 Hz), 171.1; $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.7; IR (neat): $\nu$ (cm$^{-1}$) 3495, 2938, 2897, 2843, 1738, 1464, 1240, 1026, 964; LC-MS (ESI) [M+H]$^+$: 246.26; HRMS (ESI) calcd for C$_{11}$H$_{21}$O$_3$P [M+H]$^+$ 246.1254, found 246.1259.

Diethyl (8-chlorooct-1-en-2-yl)phosphonate (3l). Pale yellow oil (89.1 mg, 79% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.30-1.35 (m, 8H), 1.41-1.48 (m, 2H), 1.50-1.56 (m, 2H), 1.73-1.79 (m, 2H), 2.20-2.26 (m, 2H), 3.50-3.53 (m, 2H), 4.03-4.11 (m, 4H), 5.74 (d, $J$ = 49.0 Hz, 1H), 6.01 (dd, $J$ = 23.0 Hz, 0.6 Hz, 1H), 32.4, 44.9, 61.7 (d, $J$ = 5.6 Hz), 129.0 (d, $J$ = 9.3 Hz), 139.1 (d, $J$ = 170.3 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.8; IR (neat): $\nu$ (cm$^{-1}$) 3474, 2938, 2897, 2843, 1464, 1242, 1053, 1026, 964; GC-MS: m/z (rel intensity) 282 (M$^+$, 0.4), 247 (100), 219 (31), 205 (39), 177 (51), 163 (27), 149 (73), 109 (80), 81 (40); HRMS (ESI) calcd for C$_{13}$H$_{26}$ClNaO$_3$P [M+Na]$^+$: 305.1044, found 305.1059.

Diethyl hepta-1,6-dien-2-ylphosphonate (3m). Pale yellow oil (68.7 mg, 74% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.30 (t, $J$ = 7.1 Hz, 6H), 1.58-1.64 (m, 2H), 2.04-2.09 (m, 2H), 2.21-2.27 (m, 2H), 4.00-4.11 (m, 4H), 4.94-5.02 (m, 2H), 5.69-5.82 (m, 2H), 6.02 (d, $J$ = 23.0 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J$ = 6.3 Hz), 26.5, 27.7 (d, $J$ = 5.4 Hz), 32.4, 44.9, 61.7 (d, $J$ = 5.6 Hz), 129.0 (d, $J$ = 9.3 Hz), 139.1 (d, $J$ = 170.3 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.7; IR (neat): $\nu$ (cm$^{-1}$) 3464, 2938, 2897, 2843, 1464, 1242, 1053, 1026, 964; LC-MS (ESI) [M+H]$^+$: 233.26; HRMS (ESI) calcd for C$_{11}$H$_{21}$NaO$_3$P [M+Na]$^+$ 255.1121, found 255.1123.

Diethyl (3-(m-tolyl)prop-1-en-2-yl)phosphonate (6b). Pale yellow oil (99.7 mg, 93% yield); $^1$H
NMR (500 MHz, CDCl₃): δ 1.27 (t, J = 7.1 Hz, 6H), 2.33 (s, 3H), 3.52 (d, J = 11.3 Hz, 2H), 3.93-4.09 (m, 4H), 5.58 (dd, J = 47.8 Hz, 1.6 Hz, 1H), 6.10 (dd, J = 22.3 Hz, 1.3 Hz, 1H), 6.98-7.05 (m, 3H), 7.18-7.21 (t, J = 7.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 16.1 (d, J = 6.4 Hz), 21.3, 38.1 (d, J = 11.6 Hz), 61.7 (d, J = 5.7 Hz), 126.4, 127.2, 128.2, 130.1, 130.6 (d, J = 9.5 Hz), 137.5 (d, J = 7.6 Hz), 137.9, 139.0 (d, J = 171.8 Hz); ³¹P NMR (202.5 MHz, CDCl₃): δ 19.1; IR (neat): ν (cm⁻¹) 3480, 2938, 2897, 2843, 1722, 1464, 1163, 1026, 966; LC-MS (ESI) [M+H]⁺: 269.31; HRMS (ESI) calcd for C₁₄H₂₁NaO₃P [M+Na]⁺ 291.1121, found 291.1139.

Diethyl (3-(p-tolyl)prop-1-en-2-yl)phosphonate (6c). Pale yellow oil (96.5 mg, 90% yield); ¹H NMR (500 MHz, CDCl₃): δ 1.27 (t, J = 7.1 Hz, 6H), 2.33 (s, 3H), 3.51 (d, J = 11.1 Hz, 2H), 3.93-4.09 (m, 4H), 5.56 (dd, J = 47.9 Hz, 1.5 Hz, 1H), 6.09 (dd, J = 22.3 Hz, 1.1 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 16.2 (d, J = 6.4 Hz), 21.0, 37.8 (d, J = 11.6 Hz), 61.7 (d, J = 5.7 Hz), 129.1, 129.2, 130.5 (d, J = 9.5 Hz), 134.5 (d, J = 7.6 Hz), 136.0, 139.2 (d, J = 171.2 Hz); ³¹P NMR (202.5 MHz, CDCl₃): δ 19.2; IR (neat): ν (cm⁻¹) 3426, 2938, 2897, 2843, 1722, 1464, 1163, 1024, 968; LC-MS (ESI) [M+H]⁺: 269.32; HRMS (ESI) calcd for C₁₄H₂₂O₃P [M+H]⁺ 269.1301, found 269.1293.

Diethyl (3-(4-(tert-butyl)phenyl)prop-1-en-2-yl)phosphonate (6d). Pale yellow oil (111.6 mg, 90% yield); ¹H NMR (500 MHz, CDCl₃): δ 1.24 (t, J = 7.1 Hz, 6H), 1.31 (s, 9H), 3.52 (d, J = 11.7 Hz, 2H), 3.90-4.08 (m, 4H), 5.61 (dd, J = 47.9 Hz, 1.5 Hz, 1H), 6.10 (dd, J = 22.3 Hz, 1.1 Hz, 1H), 7.07 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 16.2 (d, J = 6.6 Hz), 31.3, 34.4, 37.9 (d, J = 11.6 Hz), 61.7 (d, J = 5.5 Hz), 125.3, 129.0, 130.7 (d, J = 9.6 Hz), 134.5 (d, J = 7.3 Hz), 139.1 (d, J = 171.3 Hz), 149.4; ³¹P NMR (202.5 MHz, CDCl₃): δ 19.1; IR (neat): ν (cm⁻¹) 3456, 2938, 2895, 2843, 1514, 1464, 1234, 1165, 1026, 966; LC-MS (ESI) [M+H]⁺: 311.43; HRMS (ESI) calcd for C₁₇H₂₇O₃P [M+H]⁺ 311.1771, found 311.1779.

Diethyl (3-(4-methoxyphenyl)prop-1-en-2-yl)phosphonate (6e). Pale yellow oil (100.0 mg, 88% yield); ¹H NMR (500 MHz, CDCl₃): δ 1.27 (t, J = 7.1 Hz, 6H), 3.49 (d, J = 11.7 Hz, 2H), 3.80 (s, 3H), 3.94-4.08 (m, 4H), 5.62 (dd, J = 48.9 Hz, 1.5 Hz, 1H), 6.10 (dd, J = 22.7 Hz, 1.1 Hz, 1H),
6.83-6.88 (m, 2H), 7.08-7.11 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.2 (d, $J = 6.4$ Hz), 37.4 (d, $J = 11.8$ Hz), 55.3, 62.4 (d, $J = 5.6$ Hz), 113.9, 129.3 (d, $J = 7.9$ Hz), 130.4, 131.3 (d, $J = 9.8$ Hz), 138.5 (d, $J = 173.1$ Hz), 158.4; $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.1; IR (neat): $\nu$ (cm$^{-1}$) 3400, 2938, 2899, 2843, 1767, 1612, 1512, 1464, 1248, 1163, 1026, 968; LC-MS (ESI) [M+H]$^+$: 285.35; HRMS (ESI) calcd for C$_{14}$H$_{21}$NaO$_4$P [M+Na]$^+$ 307.1070, found 307.1080.

Diethyl (3-(2-chlorophenyl)prop-1-en-2-yl)phosphonate (6f). Pale yellow oil (107.1 mg, 93% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.31 (t, $J = 7.1$ Hz, 6H), 3.68 (dt, $J = 9.0$ Hz, 1.7Hz, 2H), 4.01-4.15 (m, 4H), 5.40 (dd, $J = 47.8$ Hz, 1.5 Hz, 1H), 6.10 (dd, $J = 22.3$ Hz, 1.1 Hz, 1H), 7.19-7.25 (m, 3H), 7.37-7.38 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J = 6.4$ Hz), 35.8 (d, $J = 12.2$ Hz), 61.9 (d, $J = 5.5$ Hz), 126.9, 128.4, 129.6, 130.4 (d, $J = 9.4$ Hz), 131.8, 134.5, 135.3 (d, $J = 9.7$ Hz), 136.9 (d, $J = 173.1$ Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 18.6; IR (neat): $\nu$ (cm$^{-1}$) 3478, 2938, 2897, 2843, 1464, 1250, 1024, 966; LC-MS (ESI) [M+H]$^+$: 289.28; HRMS (ESI) calcd for C$_{13}$H$_{19}$ClO$_3$P [M+H]$^+$ 289.0755, found 289.0777.

Diethyl (3-(4-bromophenyl)prop-1-en-2-yl)phosphonate (6g). Pale yellow oil (126.2 mg, 95% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.26 (t, $J = 7.1$ Hz, 6H), 3.51 (d, $J = 12.0$ Hz, 2H), 3.94-4.10 (m, 4H), 5.62 (dd, $J = 48.3$ Hz, 1.4 Hz, 1H), 6.12 (dd, $J = 22.5$ Hz, 1.2 Hz, 1H), 7.05-7.08 (m, 2H), 7.42-7.44 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.1 (d, $J = 6.3$ Hz), 37.7 (d, $J = 11.8$ Hz), 62.3 (d, $J = 6.0$ Hz), 120.5, 131.0, 131.3 (d, $J = 9.8$ Hz), 131.5, 136.5 (d, $J = 7.2$ Hz), 138.0 (d, $J = 174.2$ Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 18.5; IR (neat): $\nu$ (cm$^{-1}$) 3416, 2938, 2895, 2843, 1766, 1464, 1215, 1163, 1026, 968; LC-MS (ESI) [M+H]$^+$: 333.31; HRMS (ESI) calcd for C$_{13}$H$_{18}$BrNaO$_3$P [M+Na]$^+$ 355.0069, found 355.0077.

Diethyl (3-(4-fluorophenyl)prop-1-en-2-yl)phosphonate (6h). Pale yellow oil (103.4 mg, 95% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.26 (t, $J = 7.1$ Hz, 6H), 3.53 (d, $J = 11.7$ Hz, 2H), 3.93-4.09 (m, 4H), 5.58 (dd, $J = 47.6$ Hz, 1.6 Hz, 1H), 6.10 (dd, $J = 23.3$ Hz, 1.1 Hz, 1H), 6.98-7.01 (m, 2H), 7.14-7.16 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.1 (d, $J = 6.4$ Hz), 37.6 (d, $J = 11.8$ Hz), 62.3 (d, $J = 5.8$ Hz), 115.3 (d, $J = 21.0$ Hz), 130.8 (d, $J = 7.9$ Hz), 131.2 (d, $J = 9.7$ Hz), 133.1 (dd,
$J = 7.2$ Hz, 3.5 Hz), 138.3 (d, $J = 174.0$ Hz), 161.7 (d, $J = 243.6$ Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 18.7; $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -116.6; IR (neat): $\nu$ (cm$^{-1}$) 3422, 2938, 2897, 2843, 1464, 1223, 1026, 968; LC-MS (ESI) [M+H]$^+$: 273.32; HRMS (ESI) calcd for C$_{13}$H$_{18}$FNaO$_3$P $[\text{M+Na}]^+$: 295.0870, found 295.0880.

Diethyl (3-(4-cyanophenyl)prop-1-en-2-yl)phosphonate (6i). Pale yellow oil (109.4 mg, 98% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.25 (t, $J = 7.1$ Hz, 6H), 3.63 (d, $J = 12.8$ Hz, 2H), 3.95-4.10 (m, 4H), 5.67 (d, $J = 48.2$ Hz, 1H), 6.16 (d, $J = 22.4$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 8.1$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.0 (d, $J = 6.3$ Hz), 38.4 (d, $J = 11.9$ Hz), 62.4 (d, $J = 6.1$ Hz), 110.5, 118.7, 130.0, 132.0 (d, $J = 17.8$ Hz), 132.2, 137.1 (d, $J = 176.4$ Hz), 143.2 (d, $J = 6.3$ Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 18.5; IR (neat): $\nu$ (cm$^{-1}$) 3470, 2938, 2895, 2843, 2228, 1770, 1464, 1163, 1024, 972; LC-MS (ESI) [M+H]$^+$: 280.33; HRMS (ESI) calcd for C$_{14}$H$_{18}$NNaO$_3$P $[\text{M+Na}]^+$: 302.0917, found 302.0928.

Ethyl 4-(2-(diethoxyphosphoryl)allyl)benzoate (6j). Pale yellow oil (125.2 mg, 96% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.26 (t, $J = 7.1$ Hz, 6H), 1.39 (t, $J = 7.1$ Hz, 3H), 3.61 (d, $J = 12.3$ Hz, 2H), 3.95-4.11 (m, 4H), 4.37 (q, $J = 7.1$ Hz, 2H), 5.66 (dd, $J = 48.8$ Hz, 1.2 Hz, 1H), 6.16 (dd, $J = 22.7$ Hz, 0.9 Hz, 1H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.99 (d, $J = 8.2$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 14.3, 16.1 (d, $J = 6.4$ Hz), 38.2 (d, $J = 12.2$ Hz), 61.0, 62.7 (d, $J = 5.8$ Hz), 129.0, 129.3, 129.8, 132.0 (d, $J = 9.7$ Hz), 137.3 (d, $J = 175.9$ Hz), 142.6 (d, $J = 7.1$ Hz), 166.5; $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 18.3; IR (neat): $\nu$ (cm$^{-1}$) 3412, 2938, 2899, 2843, 1717, 1611, 1464, 1277, 1163, 1024, 970; LC-MS (ESI) [M+H]$^+$: 327.40; HRMS (ESI) calcd for C$_{16}$H$_{24}$O$_5$P $[\text{M+H}]^+$: 327.1356, found 327.1356.

Diethyl (3-(2,6-dimethylphenyl)prop-1-en-2-yl)phosphonate (6k). Pale yellow oil (101.5 mg, 90% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.38 (t, $J = 7.1$ Hz, 6H), 2.21 (s, 6H), 3.52 (d, $J = 5.7$ Hz, 2H), 4.10-4.21 (m, 4H), 5.10 (dd, $J = 48.5$ Hz, 1.7 Hz, 1H), 5.96 (dd, $J = 22.7$ Hz, 1.7 Hz, 1H), 7.03-7.09 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.4 (d, $J = 6.2$ Hz), 19.6, 31.4 (d, $J = 11.7$ Hz), 61.9 (d, $J = 5.7$ Hz), 126.6, 128.0, 128.2 (d, $J = 9.8$ Hz), 134.0 (d, $J = 11.8$ Hz), 136.7 (d, $J =
171.4 Hz), 137.1; $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.4; IR (neat): v (cm$^{-1}$) 3480, 2938, 2895, 2843, 1722, 1464, 1244, 1170, 1024, 964; LC-MS (ESI) [M+H]$^+$/: 283.36; HRMS (ESI) calcd for C$_{15}$H$_{23}$NaO$_3$P [M+Na]$^+$ 305.1277, found 305.1279.

![Structure of Diethyl (3-naphthalen-1-yl)prop-1-en-2-ylphosphonate](image)

**Diethyl (3-naphthalen-1-yl)prop-1-en-2-ylphosphonate (6l).** Pale yellow oil (119.2 mg, 98% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.36 (t, $J$ = 7.1 Hz, 6H), 3.99 (d, $J$ = 7.8 Hz, 2H), 4.09-4.20 (m, 4H), 5.26 (d, $J$ = 48.4 Hz, 1H), 6.04 (d, $J$ = 22.7 Hz, 1H), 7.35 (d, $J$ = 6.9 Hz, 1H), 7.42-7.49 (m, 3H), 7.78 (d, $J$ = 8.2 Hz, 1H), 7.85-7.89 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.3 (d, $J$ = 6.3 Hz), 35.2 (d, $J$ = 12.0 Hz), 62.0 (d, $J$ = 5.7 Hz), 122.4, 125.4, 125.6, 125.9, 127.6, 128.2, 128.6, 130.3 (d, $J$ = 9.4 Hz), 131.9, 133.6 (d, $J$ = 10.1 Hz), 133.8, 138.2 (d, $J$ = 172.7 Hz), $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.1; IR (neat): v (cm$^{-1}$) 3474, 2936, 2900, 2857, 1464, 1242, 1024, 964; LC-MS (ESI) [M+H]$^+$/: 305.14; HRMS (ESI) calcd for C$_{16}$H$_{19}$NaO$_3$P [M+Na]$^+$ 327.1121, found 327.1138.

![Structure of Dipropyl (3-phenylprop-1-en-2-yl)phosphonate](image)

**Dipropyl (3-phenylprop-1-en-2-yl)phosphonate (6m).** Pale yellow oil (107.2 mg, 95% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.24 (d, $J$ = 6.2 Hz, 6H), 1.32 (d, $J$ = 6.2 Hz, 6H), 3.54 (d, $J$ = 10.4 Hz, 2H), 4.61-4.70 (m, 2H), 5.46 (dd, $J$ = 48.0 Hz, 1.7 Hz, 1H), 6.09 (dd, $J$ = 22.5 Hz, 1.3 Hz, 1H), 7.17-7.31 (m, 5H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 23.7 (d, $J$ = 4.8 Hz), 24.0 (d, $J$ = 3.8 Hz), 38.2 (d, $J$ = 11.4 Hz), 70.5 (d, $J$ = 6.1 Hz), 126.4, 128.4, 129.5, 129.6 (d, $J$ = 9.7 Hz), 137.8 (d, $J$ = 8.2 Hz), 140.6 (d, $J$ = 174.1 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 16.8; IR (neat): v (cm$^{-1}$) 3462, 2936, 2901, 2845, 2359, 1464, 1385, 1252, 1107, 982; GC-MS: m/z (rel intensity) 282 (M$^+$, 10), 240 (21), 198 (100), 181 (26), 163 (25), 116 (94), 91 (21); HRMS (ESI) C$_{16}$H$_{19}$O$_3$PNa [M+Na]$^+$ 305.1277, found 305.1290.

![Diethyl (3-phenylbut-1-en-2-yl)phosphonate](image)

**Diethyl (3-phenylbut-1-en-2-yl)phosphonate (7).** Pale yellow oil (30.0 mg, 28% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.09 (t, $J$ = 7.1 Hz, 3H), 1.23 (t, $J$ = 7.1 Hz, 3H), 1.47 (d, $J$ = 7.2 Hz, 3H), 3.63-3.71 (m, 1H), 3.81-3.87 (m, 1H), 3.88-4.01 (m, 3H), 5.88 (dd, $J$ = 48.5 Hz, 1.2 Hz, 1H), 6.21 (d, $J$ = 23.1 Hz, 1H), 7.18-7.23 (m, 3H), 7.27-7.30 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 16.0 (d, $J$ = 7.0 Hz), 16.2 (d, $J$ = 6.5 Hz), 21.3 (d, $J$ = 6.8 Hz), 41.1 (d, $J$ = 11.6 Hz), 61.6 (d, $J$ = 5.5 Hz), 126.4, 127.6, 128.3, 129.1 (d, $J$ = 9.2 Hz), 143.68 (d, $J$ = 4.4 Hz), 143.70 (d, $J$ = 169.7 Hz); $^{31}$P NMR (202.5 MHz, CDCl$_3$): $\delta$ 19.2; **Diethyl (4-phenylbut-1-en-2-yl)phosphonate (3g).** Pale yellow oil (17.2 mg, 16% yield); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.34 (t, $J$ = 7.1 Hz, 6H),
2.53-2.59 (m, 2H), 2.83-2.86 (m, 2H), 4.03-4.15 (m, 4H), 5.75 (dd, J = 48.8 Hz, 1.5 Hz, 1H), 6.06 (dd, J = 23.0 Hz, 1.1 Hz, 1H), 7.18-7.23 (m, 3H), 7.27-7.30 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 16.3 (d, J = 6.3 Hz), 33.9 (d, J = 11.1 Hz), 34.3 (d, J = 5.4 Hz), 61.8 (d, J = 5.9 Hz), 126.0, 128.3, 128.4, 129.6 (d, J = 9.5 Hz), 138.5 (d, J = 171.0 Hz), 141.1; \(^{31}\)P NMR (202.5 MHz, CDCl\(_3\)): \(\delta\) 19.5; LC-MS (ESI) [M+H]\(^+\): 269.31; IR (neat): \(\nu\) (cm\(^{-1}\)) 3431, 2938, 2897, 2843, 1463, 1247, 1055, 1028, 962; HRMS (ESI) calcd for C\(_{14}\)H\(_{21}\)NaO\(_3\)P [M+Na]\(^+\) 291.1121, found 291.1128.

**Diethyl (1,3-diphenylprop-1-en-2-yl)phosphonate (11).** Pale yellow oil (128.0 mg, 97% yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.03 (t, J = 7.1 Hz, 6H), 3.69-3.89 (m, 6H), 7.05 (d, J = 47.9 Hz, 1H), 7.21-7.34 (m, 8H), 7.48 (d, J = 7.4 Hz, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 15.9 (d, J = 6.8 Hz), 42.0 (d, J = 12.1 Hz), 61.5 (d, J = 5.8 Hz), 126.4, 127.7, 128.1, 128.4, 129.1 (d, J = 1.5 Hz), 129.4, 130.5 (d, J = 173.6 Hz), 136.2 (d, J = 7.4 Hz), 138.8 (d, J = 5.3 Hz), 145.0 (d, J = 9.3 Hz); \(^{31}\)P NMR (202.5 MHz, CDCl\(_3\)): \(\delta\) 17.4; IR (neat): \(\nu\) (cm\(^{-1}\)) 3420, 2936, 2899, 2843, 2359, 1464, 1240, 1026, 966; GC-MS: m/z (rel intensity) 330 (M\(^+\), 31), 301 (10), 273 (17), 239 (10), 191 (100), 165 (22), 129 (12), 115 (59), 91 (41); HRMS (ESI) C\(_{19}\)H\(_{24}\)O\(_3\)P [M+H]\(^+\) 331.1458, found 331.1446.

**Diethyl (1,3-diphenylprop-1-en-2-yl)phosphonate (15).** Pale yellow oil (88.4 mg, 67% yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.15 (t, J = 7.1 Hz, 6H), 3.83-3.92 (m, 4H), 3.98-4.05 (m, 2H), 7.18-7.42 (m, 10H), 7.75 (d, J = 24.8 Hz, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 16.0 (d, J = 6.5 Hz), 33.6 (d, J = 9.2 Hz), 61.7 (d, J = 5.6 Hz), 126.2, 128.2, 128.4, 128.55, 128.6 (d, J = 176.9 Hz), 128.7, 129.0, 135.1 (d, J = 23.2 Hz), 138.2 (d, J = 1.6 Hz), 144.9 (d, J = 12.1 Hz); \(^{31}\)P NMR (202.5 MHz, CDCl\(_3\)): \(\delta\) 21.3; IR (neat): \(\nu\) (cm\(^{-1}\)) 3462, 2936, 2902, 2845, 2359, 1464, 1250, 1024, 962; GC-MS: m/z (rel intensity) 330 (M\(^+\), 50), 301 (10), 273 (17), 239 (12), 191 (100), 165 (25), 129 (11), 115 (59), 91 (44); HRMS (ESI) C\(_{19}\)H\(_{24}\)O\(_3\)P [M+H]\(^+\) 331.1458, found 331.1433.

**Diethyl (1-bromo-2-methylprop-1-en-1-yl)phosphonate (16a).** Pale yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.35 (t, J = 7.1 Hz, 6H), 2.09 (d, J = 2.2 Hz, 3H), 2.30 (d, J = 2.9 Hz, 3H), 4.06-4.18 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 16.1 (d, J = 6.6 Hz), 23.3 (d, J = 3.9 Hz), 28.0 (d, J = 13.9 Hz), 62.5 (d, J = 5.4 Hz), 106.5 (d, J = 207.5 Hz), 156.0 (d, J = 17.0 Hz); \(^{31}\)P NMR (202.5 MHz, CDCl\(_3\)): \(\delta\) 9.7; IR (neat): \(\nu\) (cm\(^{-1}\)) 3462, 2934, 2903, 2845, 1602, 1464, 1253, 1024, 970;
Diethyl (3-methyl-1-phenylbut-2-en-2-yl)phosphonate (17). Pale yellow oil (104.9 mg, 93% yield); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.19 (t, \(J = 7.1\) Hz, 6H), 1.89 (d, \(J = 2.5\) Hz, 3H), 2.23 (d, \(J = 3.3\) Hz, 3H), 3.69 (d, \(J = 17.7\) Hz, 2H), 3.82-3.99 (m, 4H), 7.14-7.27 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 16.1 (d, \(J = 6.4\) Hz), 23.2 (d, \(J = 19.2\) Hz), 23.9 (d, \(J = 7.7\) Hz), 35.8 (d, \(J = 12.0\) Hz), 61.1 (d, \(J = 5.6\) Hz), 122.2 (d, \(J = 178.8\) Hz), 125.8, 128.07, 128.14, 139.7 (d, \(J = 1.8\) Hz), 153.3 (d, \(J = 12.0\) Hz); \(^{31}\)P NMR (202.5 MHz, CDCl\(_3\)): \(\delta\) 20.8; IR (neat): \(\nu\) (cm\(^{-1}\)) 3462, 2936, 2899, 2845, 2359, 1464, 1229, 1026, 959; GC-MS: \(m/z\) (rel intensity) 282 (M\(^+\), 63), 253 (10), 225 (15), 191 (13), 157 (10), 143 (88), 129 (100), 115 (18), 91 (34); HRMS (ESI) C\(_{15}\)H\(_{24}\)O\(_3\)P [M+H\(^+\)]: 283.1458, found 283.1448.

Diethyl (8-chlorooctan-2-yl)phosphonate (20f). Colorless oil (62.2 mg, 73% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.15 (dd, \(J = 18.7\) Hz, 7.1Hz, 3H), 1.29-1.37 (m, 9H), 1.40-1.48 (m, 3H), 1.72-1.81 (m, 5H), 3.52 (t, \(J = 6.7\) Hz, 2H), 4.05-4.14 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 13.1 (d, \(J = 5.0\) Hz), 16.5 (d, \(J = 5.8\) Hz), 26.6, 27.1 (d, \(J = 13.4\) Hz), 28.6, 29.7 (d, \(J = 3.7\) Hz), 30.6 (d, \(J = 139.9\) Hz), 32.5, 45.0, 61.4 (dd, \(J = 6.7\) Hz, 4.5Hz); \(^{31}\)P NMR (202.5 MHz, CDCl\(_3\)): \(\delta\) 35.0; IR (neat): \(\nu\) (cm\(^{-1}\)) 3462, 2938, 2899, 2843, 1464, 1230, 1056, 1028, 960; LC-MS (ESI) [M+H\(^+\)]: 285.23; HRMS (ESI) C\(_{12}\)H\(_{26}\)ClNaO\(_3\)P [M+Na\(^+\)]: 307.1200, found 307.1202.

References of known compounds

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References


$^1$H, $^{13}$C, $^{31}$P, $^{19}$F NMR spectra of new compounds

\[
\begin{align*}
\text{PO(Oi-Pr)$_2$} \\
\text{Cl} \\
\end{align*}
\]

(1f)
$\text{PO(OEt)}_2$ (Et)

$\text{CN (3j)}$

$\text{PO(OEt)}_2$

$\text{CN}$
\begin{align*}
\text{PO}(\text{OE})_2 & \quad (6b) \\
\text{PO}(\text{OE})_2 & \quad \text{Me} \\
\text{PO}(\text{OE})_2 & \quad \text{Me}
\end{align*}
$\text{Et}_2\text{C} - \text{C} = \text{PO(OEt)}_2$
$\text{BnPO(OEt)}_2$

$\text{BnPO(O-i-Pr)}_2$ (6m)
$PO(OE)_2$

Ph Ph

PO(OE)$_2$

Ph Ph
$\text{PO(OEt)}_2$

$\text{Me}_{12} \text{Cl} \; (20f)$
\text{Me} \begin{array}{c}
\text{PO(OEt)_2} \\
\text{Cl}
\end{array}